

Communications

New Routes to Organodecaborane Polymers via Ruthenium-Catalyzed Ring-Opening Metathesis Polymerization

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Received October 1, 2003

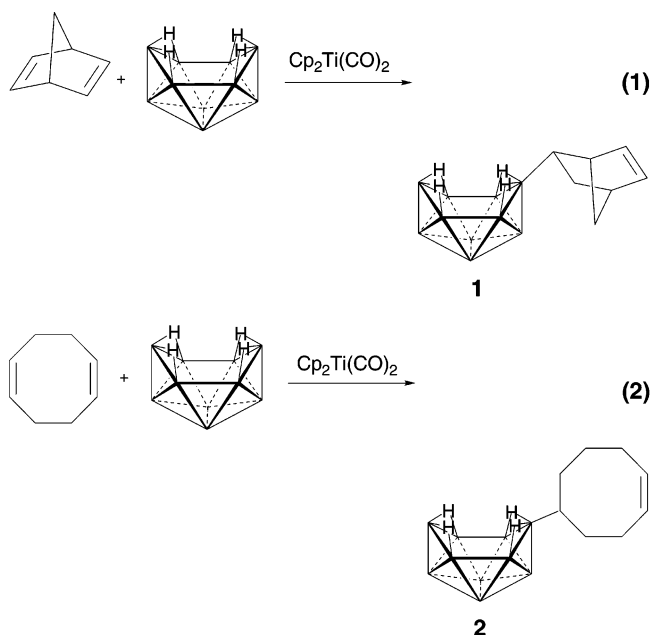
Summary: The compounds 6-(norbornenyl)decaborane and 6-(cyclooctenyl)decaborane were synthesized in > 95% yields by the titanium-catalyzed reaction of norbornadiene and cyclooctadiene with decaborane. Ring-opening metathesis polymerization of these monomers employing either first- or second-generation Grubbs catalysts produced the corresponding poly(6-(norbornenyl)decaborane) and poly(6-(cyclooctenyl)decaborane) polymers with $M_n > 30$ kDa and polydispersities between 1.1 and 1.8.

As a result of our interest in the design of new polymeric precursors to non-oxide ceramics, we have been investigating the development of new general metal-catalyzed methods for the synthesis of polyborane polymers. We have previously shown¹ that the $\text{Cp}_2\text{-ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system² efficiently polymerizes 6-(hexenyl)decaborane to poly(6-(hexenyl)decaborane), and our report was the first application of such a catalyst for an alkenylpolyborane polymerization. In this communication, we report an alternative, and potentially more versatile, route to polyborane polymers that employs ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) reactions.

Metal-catalyzed reactions, using either "Schrock-type" $\text{M}(\text{NAr})(=\text{CHR})(\text{OR}')_2\cdot\text{L}$ ($\text{M} = \text{Mo}, \text{W}$) or "Grubbs-type" $\text{Cl}_2(\text{PCy}_3)\text{Ru}(\text{=CHPh})\text{L}$ ($\text{L} = \text{PCy}_3$ (**I**), IMesH_2 (**II**)) catalysts have been applied to the ROMP of a variety of ring systems, including norbornenes, norbornadienes, 7-oxanorbornenes, cyclooctatetraenes, and cyclooctadienes, and can generate organic polymers with highly monodispersed and controllable molecular weights.³ Recently, Chung also showed that $\text{WCl}_6/\text{Me}_4\text{Sn}$ catalyzes the ROMP of 9-BBN-norbornene to poly(9-BBN-norbornene) and that $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ catalyzes the formation of poly(5-cyclooctenyl)diethylborane by ROMP of (5-cyclooctenyl)diethylborane.⁴ These prior results suggested to us that metal-catalyzed ROMP reactions of polyborane-functionalized cyclic

olefins could be employed as a route to new classes of poly(organopolyboranes).

As shown in eqs 1 and 2, the high-yield syntheses of the key decaboranyl-substituted norbornene and cyclooctene monomers were achieved by employing the titanium-catalyzed⁵ reaction of decaborane with norbornadiene and cyclooctadiene, respectively.



Typical conditions involved the reaction of a large excess of the olefin with decaborane in the presence of ~3 mol % catalyst at 90 °C for 72 h. The products were easily isolated in pure form and excellent yields (**1**, 98%; **2**, 96%) from the metal catalyst by filtration through silica gel. Both products have spectral and analytical data consistent with structures proposed in the equations.⁶ The ¹H NMR spectrum of the product of the reaction with norbornadiene indicated the formation of

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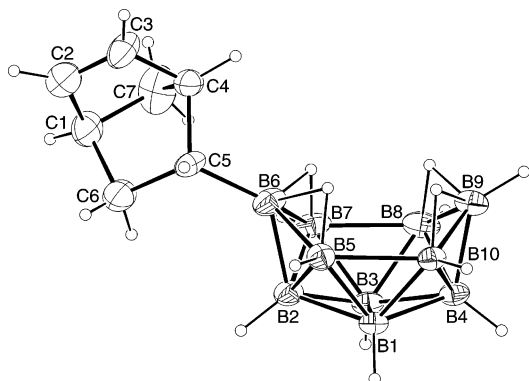
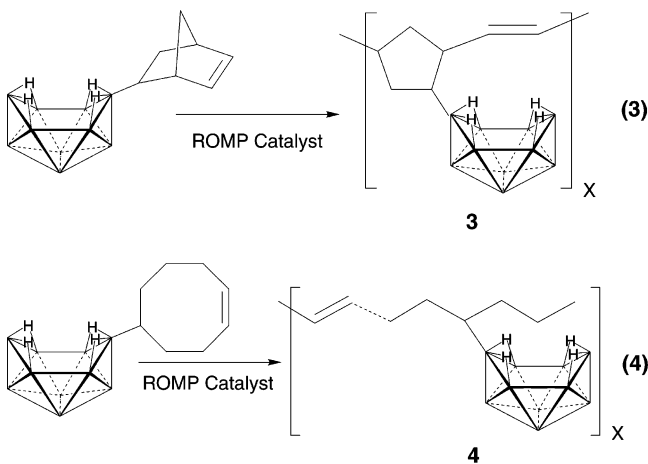


Figure 1. ORTEP drawing of the structure of *exo*-1.

both the *exo* and *endo* isomers in a 4:1 ratio. The *exo* isomer of **1** was isolated by crystallization from toluene. As shown in Figure 1, a single-crystal X-ray determination⁷ confirmed a 6-substituted norbornenyl-decaborane structure resulting from the titanium-catalyzed hydroboration of the norbornadiene C5–C6 double bond.

Because of their air stability and tolerance to various functional groups, Grubbs-type ROMP catalysts appear to be ideal candidates for the syntheses of polyborane polymers. Indeed, ROMP of monomers **1** and **2** with either the first-generation (**I**) or second-generation (**II**) catalyst readily yielded the poly(organodecaborane) polymers shown in eqs 3 and 4.



Polymerization reactions were carried out at room temperature for 1 h, in a minimum of CH_2Cl_2 solvent using 1 or 2 mol % of the catalysts. After reaction termination, the polymers were isolated by column chromatography using pentane and CH_2Cl_2 eluents. Following precipitation in pentane, the polymers were

(6) For *exo*-1: ^{11}B NMR (C_6D_6) δ 29.2 (s, 1, B6), 12.3 (d, 2, B1,3), 10.5 (d, 1, B9), 2.8 (d, 2, B5,7), -1.5 (d, 2, B8,10), -31.9 (d, 1, B2), -36.4 (d, 1, B4); ^1H NMR (C_6D_6) δ 6.17–5.89 (m, 2H), 2.74 (d, 2H), 1.67 (m, 2H), 1.46 (m, 2H), 1.37 (d, 1H), -2.1 (br, 4BHB). Anal. Calcd for $\text{C}_7\text{B}_{10}\text{H}_{22}$: C, 39.22; H, 10.34. Found: C, 38.55; H, 10.10. For **2**: ^{11}B NMR (C_6D_6) δ 29.0 (s, 1, B6), 10.5 (d, 2, B1,3), 8.7 (d, 1, B9), 1.0 (d, 2, B5,7), -3.5 (d, 2, B8,10), -34.0 (d, 1, B2), -38.3 (d, 1, B4); ^1H NMR (C_6D_6) δ 5.79–5.52 (m, 2H), 2.28 (m, 2H), 2.12 (m, 2H), 1.78 (m, 6H), 1.63 (m, 1H), -2.1 (br, 4BHB). Anal. Calcd for $\text{C}_8\text{B}_{10}\text{H}_{26}$: C, 41.71; H, 11.37. Found: C, 41.29; H, 11.67.

(7) Crystal data for *exo*-1: $\text{C}_7\text{B}_{10}\text{H}_{22}$, $M = 214.35$, space group $P2_1/c$, $a = 10.906(2)$ Å, $b = 13.048(2)$ Å, $c = 10.811(2)$ Å, $\beta = 117.287(3)^\circ$, $V = 1367.3(5)$ Å³, $Z = 4$, $D_c = 1.041$ g/cm³, $\mu(\text{Mo K}\alpha) = 0.47$ cm⁻¹, 230 parameters refined with 2430 unique reflections to $R_1 = 0.0770$. The norbornene moiety was disordered through two orientations, and the two structures were refined with populations of 0.70 and 0.30.

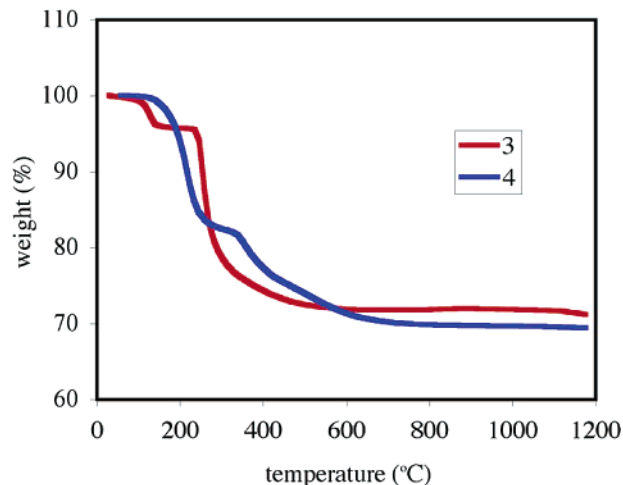


Figure 2. TGA curves of 32 kDa **3** and **4** to 1200 °C under argon at a heating rate of 10 °C/min.

Table 1. Polymerization of **1** with Grubbs Catalysts

cat.	[M]/[Ru]	conversn (%)	yield (%)	M_n	M_w	PDI
I	101	94.7	89.4	31 200	34 970	1.12
I	53	88.2	85.9	19 200	21 080	1.10
II	111	94.0	86.6	31 950	52 050	1.63
II	58	89.2	89.7	23 660	33 150	1.40

Table 2. Polymerization of **2** with Grubbs Catalysts

cat.	[M]/[Ru]	conversn (%)	yield (%)	M_n	M_w	PDI
I	95	63.4	80.9	12 500	16 400	1.31
I	42	56.0	81.0	6 230	7 820	1.26
II	117	80.0	96.1	32 580	57 730	1.77
II	58	73.4	90.8	21 150	29 350	1.40

isolated as air-stable white solids that were readily soluble in CH_2Cl_2 and THF. The ^1H NMR spectra of the polymers show, in addition to the resonances characteristic of their organo backbone fragments,⁸ two separate intensity 2 decaborane bridging-proton resonances consistent with retention of the C_s symmetry of the monomer. Their ^{11}B NMR spectra are, as expected, broader than those of the monomers but still have spectral patterns characteristic of a 6-substituted decaborane.⁵

Both the **I** and **II** catalysts polymerized **1** efficiently, giving $\sim 90\%$ conversions in the 1 h reaction time (Table 1). For **2**, the second-generation catalyst **II** was more active, resulting in 80.0% and 73.4% conversions (Table 2), compared to the 63.4% and 56.0% conversions observed for comparable reactions catalyzed by **I**.^{9a,b} Molecular weight studies in THF by size exclusion chromatography employing both multiangle light scat-

(8) For **3**: ^{11}B NMR (CD_2Cl_2) δ 30.1 (s, 1, B6), 12.4 (d, 3, B1,3 and B9), 3.3 (d, 2, B5,7), -0.8 (d, 2, B8,10), -31.5 (d, 1, B2), -36.3 (d, 1, B4); ^1H NMR (CD_2Cl_2) δ 5.30 (m, CH), 2.64 (m, CH), 1.99 (m, CH), 1.81 (m, CH), 1.55 (s, CH), 1.26 (m, CH), -1.6 (br, 2BHB), -2.0 (br, 2BHB). Anal. Calcd for $\text{C}_7\text{B}_{10}\text{H}_{22}$: C, 39.22; H, 10.34. Found: C, 40.28; H, 10.79. For **4**: ^{11}B NMR δ 28.1 (s, 1, B6), 11.6 (b, 3, B1,3 and B9), 2.5 (d, 2, B5,7), -1.7 (d, 2, B8,10), -32.2 (d, 1, B2), -36.8 (d, 1, B4); ^1H NMR (CD_2Cl_2) δ 5.44–5.25 (m, 2H), 2.03 (s, 4H), 1.54 (m, 6H), 1.42 (s, 1H), -1.7 (br, 2BHB), -2.0 (br, 2BHB). Anal. Calcd for $\text{C}_8\text{B}_{10}\text{H}_{26}$: C, 41.71; H, 11.37. Found: C, 42.25; H, 11.34.

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tering and DRI detectors showed that molecular weights with M_n in excess of 30 kDa can be readily obtained with polydispersities (PDI's) between 1.1 and 1.8. As found for other ROMP reactions employing these catalysts, the molecular weights of both **3** and **4** were observed to increase with an increase in the monomer/catalyst ratio.⁹

As shown in Figure 2, TGA studies of samples of **3** and **4** (each having M_n values of ~32 kDa) indicated that for both polymers weight loss begins near 100 °C and is essentially complete for **3** by 500 °C and for **4** by 700 °C to give final char yields of 72% and 70%, respectively. Given that DSC studies show that the T_g 's of both polymers are in the 65–70 °C range, these polymers have excellent potential for applications requiring molten processing. We will report full details of the ceramic conversions and the properties of the derived ceramics in future publications.

In summary, the results presented above clearly demonstrate that ruthenium-catalyzed ROMP reactions are important new methods for the systematic formation of polyborane polymers. Since ruthenium-based ROMP catalysts work with a wide variety of functionalized olefins, these reactions have excellent potential for the production of much more complex poly(organopolyborane) polymers and copolymers than are possible with our previously reported zirconium-catalyzed polymerizations.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, the Air Force Office of Scientific Research, and the National Science Foundation for financial support.

Supporting Information Available: A CIF file for the crystallographic data of *exo-1*. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0342107